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A Best-evidence Review of Bio-based Plasticizer and the Effects on the Mechanical Properties of PLA

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Polylactic Acid (PLA) plastics are currently used as food packaging material, textiles, and engineering plastics. However, PLA has its weaknesses, such as high brittleness and low toughness, limiting its application. Therefore, the epoxidized vegetable oil is used as a bio-based plasticizer to enhance the mechanical properties of PLA. Recently, many studies in developing bio-based plasticizers were recognized among researchers to replace petroleum-based plasticizers such as phthalate compound, which is known toxic and cause harmful effects on human health and the environment. This review aims to give a clear insight into the impact of bio-based plasticizers blended with PLA. The blends significantly influence the mechanical properties such as tensile strength (MPa) elongation at break (%) and the impact energy (kJ/m^2). The bio-based plasticizers discussed in the study include Karanja Oil, Rubber Seed Oil, Palm Oil, and a mixture of Palm Oil with Rubber Seed Oil. Bio-based plasticizers are made from renewable and biodegradable resources, reducing the dependency on petroleum-based plasticizers, resulting in fewer greenhouse gas emissions. Notably, bio-based plasticizers can also expedite plastic biodegradability. This review concludes a bio-based plasticizer blended with PLA improves the elongation at break and impact energy up to 16 % and 35 %, respectively. In contrast, it is also lowering about 15 % of tensile strength. This trade-off advantageously benefits the flexibility and durability of PLA.

1. Introduction

Inefficient disposal of plastic waste causes environmental issues such as air pollution, water pollution, and soil contamination. The plastic waste in the surroundings does not naturally degrade by itself. Plastic degradation in the soil is prolonged, requiring 50 y or more for plastic to degrade entirely (Webb et al., 2013). Figure 1 illustrates the exposure that consequences of burning and disposing of plastic waste into the environment.
A massive percentage of plastic waste ends up as litter in the aquatic environment. The causes are mainly easy to occur from land sources such as land littering and sewage waste. The wreckage is primarily found in large pieces and micro-particles (Pawar et al., 2016). Marine birds are endangered species by ingesting plastic objects mistaken for food (Webb et al., 2013). There have been many species being affected, such as marine birds, sea turtles, and sharks. These animals sometimes become caught in plastic waste, resulting in severe injury, restricting motion, preventing animals from eating correctly, and making breathing difficult.
Other than plastic degradation, the incineration process of plastic waste leads to air pollution, which emits soot, solid residue ash, and toxic gases that cause human health problems. A few research claims that soot and solid residual ash have a high potential for causing adverse health effects and environmental impacts, especially volatile organic compounds (VOCs) (Verma et al., 2016), smoke/soot (Hafidzal et al., 2018), and polycyclic aromatic hydrocarbons (PAHs) (Razak et al., 2021a) NO_2, CO_2, CO, and polychlorinated biphenyls (PCBs) (Razak et al., 2021b). These hazardous gases lead to an increased risk of heart disease, deteriorate respiratory issues such as asthma, emphysema, rashes, nausea, or headaches, and harms the nervous system (João et al., 2020).

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Despite the advantages of PLA, such as high mechanical strength, transparency, composability, and safety, PLA is also known for its poor characteristics, such as high brittleness and low toughness, restricting its usage (Thuy et al., 2018). Thus, a modification is needed to improve the mechanical properties of PLA. As a result, many research works have been carried out to enhance mechanical performance by adding plasticizers into polymer matrices (Ali et al., 2016).

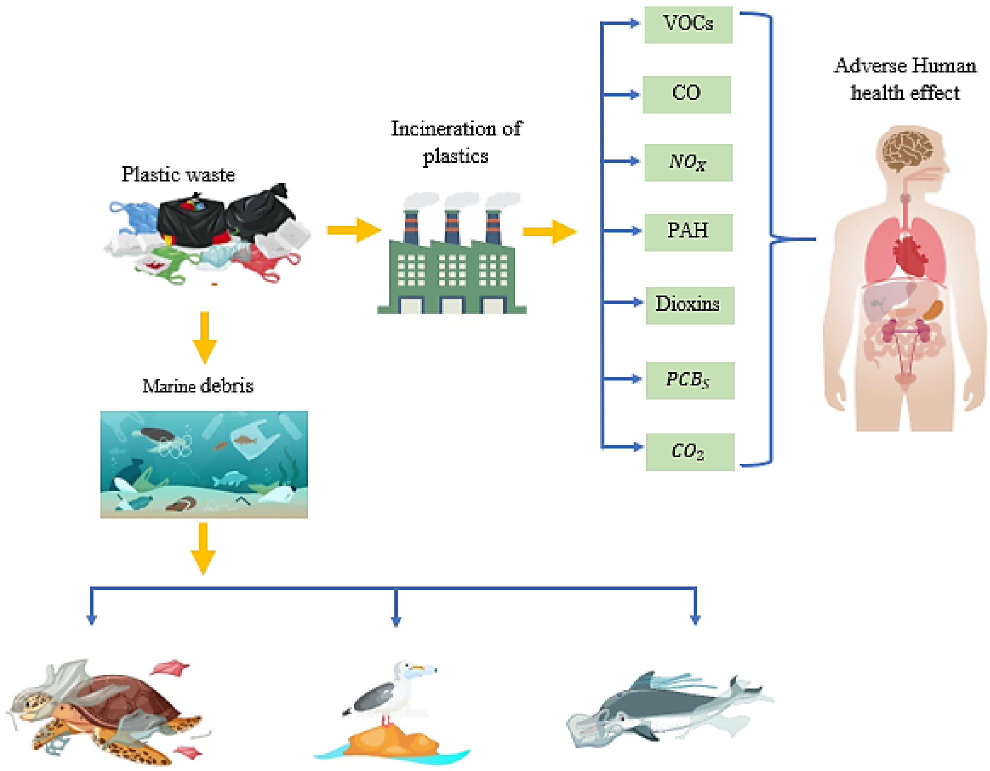


Figure 1: Exposure from plastic waste burning and disposal waste towards the human and marine environment. Adapted from (João et al., 2020)

Plasticizers play an essential role to increases the flexibility, durability, and workability of the PLA (Al-Mulla et al., 2010). Many theories have explained plasticizers' mechanism and action on polymers: lubricity theory, gel theory, and free volume theory, as shown in Table 1. Three theories of plasticizers concluded (Chieng et al., 2014). Plasticizers as lubrication are the first theory. Plasticizer minimizes friction and makes it easier to move from one place to another. Gel theory is the second theory. Plasticizers promote gel characteristics in polymer interaction, such as hydrogen bond and Van der Waals. Subsequently causing a reduction in polymer gel structure and enhanced flexibility. For free volume theory, when a plasticizer is added, the polymer molecule of the plasticizer moves more freely, causing the free volume of the polymer to increase, making it more flexible and has rubbery characteristics (Voirin et al., 2016). These advantages indicate that the biobased plasticizer is the best substitute for traditional plasticizers.
The most significant plasticizer production is petroleum-based, called phthalates compounds (Jia et al., 2018). It is reported that almost 50 % of all phthalate world production is Di-(2-ethylhexyl) (DEHP) (Voirin et al., 2016). DEHP, a petroleum-based plasticizer, is not easily degraded, is toxic to human health (Cai et al., 2020), and causes ecological dangers (Suzuki et al., 2018). Therefore, researchers are currently focusing more on natural and biodegradable (Haryono et al., 2017) plasticizers derived from epoxidized vegetable oil to replace petroleum-based plasticizers (Hosney et al., 2018), called a bio-based plasticizers.
Vegetable oil is a food purposed towards humankind that is highly valuable for other use. Therefore, a bio-based plasticizer recommended by this study is waste cooking oil (WCO) as the feedstock. A similar finding in (Cai et al., 2020). WCO has excellent benefits such as low cost, being more accessible to purchase, and being environmentally safe. Besides, recycling WCO's also tackles improper waste disposal, creating environmental hazards (Suzuki et al., 2018).

Table 1: Plasticizers theories (Voirin et al., 2016)

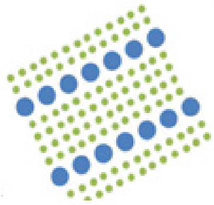
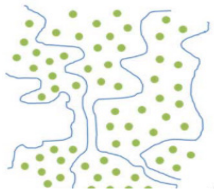
	Lubricity theory	Gel theory	Free volume theory
Mechanism	Plasticizer spreads into the polymer chains	Plasticizer works by breaking down polymer linkages and interactions	It increases the free volume of the polymer
	Minimizing intermolecular friction	Weakening hydrogen bonding, Van der Waals	Polymer molecules move more freely
Free Volumes			
	Plasticizer	Polymer	Bonding forces

Table 2: Mechanical properties of EKO, EeRSO, EPO, and EPSO

Authors	Vegetable Oil	Blending ratio		Sample characterization		
		Polymer	Plasticizers	Tensile strength (MPa)	Elongation at break (%)	Impact energy (kJ/m^2)
(Garcia-Garcia et al., 2020)	Epoxidized Karanja Oil (EKO)	PLA (100 %)	-	44 – 48	5 – 9	34 – 38
		PLA (99 %)	EKO (1.0 %)	43 – 47	8 – 12	35 – 39
		PLA (97.5 %)	EKO (2.5 %)	42 – 46	9 – 13	37 – 41
		PLA (95 %)	EKO (5 %)	41 – 45	12 – 16	49 – 53
		PLA (90 %)	EKO (10 %)	40 – 44	8 – 12	47 – 51
		Standard Method		ASTM D882-01		ISO 197:1993
(Thuy et al., 2018)	Epoxidized Rubber Seed Oil (EeRSO)	PLA (100 %)	-	55 – 59	4 – 8	0.0091 – 0.0095
		PLA (97.5 %)	EeRSO (2.5 %)	42 – 46	5 – 9	0.0153 – 0.0157
		PLA (95 %)	EeRSO (5.0 %)	34 – 38	14 – 18	0.0180 – 0.0184
		PLA (92.5 %)	EeRSO (7.5 %)	32 – 36	12 – 16	0.0187 – 0.0191
		PLA (90 %)	EeRSO (10 %)	27 – 31	6 – 10	0.0166 – 0.0170
		Standard Method		ASTM D638		ASTM D4812
(Chieng et al., 2014)	Epoxidized Palm Oil (EPO) and a mixture of Epoxidized Palm and Soybean Oil (EPSO)	PLA	-	55 – 58	3 - 8	-
		PLA (99 %)	EPO (1 %)	58 – 61	18 - 20	
		PLA (97 %)	EPO (3 %)	43 – 46	83 - 85	
		PLA (95 %)	EPO (5 %)	31 – 34	114.4	
		PLA (93 %)	EPO (7 %)	30 – 33	85 - 87	
		PLA (90 %)	EPO (10 %)	28 – 31	82 - 84	
		PLA (99 %)	EPSO (1 %)	60 – 63	42 - 44	
		PLA (97 %)	EPSO (3 %)	54 – 57	152 - 154	
		PLA (95 %)	EPSO (5 %)	35 – 38	220.5	
		PLA (93 %)	EPSO (7 %)	33 – 37	225 - 227	
		PLA (90 %)	EPSO (10 %)	30 – 33	161 - 163	
		Standard Method		ASTM D638		-

However, there are limited studies of using WCO based plasticizers blended with PLA. Thus, this paper fulfills the gaps. The report aims to review the effect of bio-based plasticizer blended with PLA mechanical properties such as tensile strength (MPa) elongation at break (%), and the impact energy (kJ/m^2) are analyzed using different types of bio-based plasticizers. The highlighted bio-based plasticizer in this paper covers rubber seed oil (RSO), Karanja oil (KO), palm oil (PO), and a mixture of palm oil with soybean oil (PSO).

Table 2 depicts the mechanical properties of plasticized PLA from literature. The mechanical properties observed are tensile strength, elongation at break, and impact energy. Four types of vegetable oil are reviewed; Epoxidized Karanja Oil (EKO), Epoxidized Palm Oil (EPO), Epoxidized Palm and Soybean Oil (EPSO), and Epoxidized Rubber Seed Oil (EeRSO). The difference blending ratio of plasticizers such as 1 %, 2.5 %, 3 %, 5

%, 7 %, 7.5 %, and 10 % with PLA to obtain the optimal blends maximizing the elongation at break and impact energy.

2. Mechanical properties

Figure 2 portrays the tensile strength profile for bio-plasticizers, including the epoxidized Karanja oil (EKO) (Garcia-Garcia et al., 2020), epoxidized palm oil (EPO), a mixture of epoxidized palm oil and soybean oil (EPSO) (Chieng et al., 2014), and epoxidized rubber seed oil (EeRSO) (Thuy et al., 2018). However, no data is provided in the articles for 1 % of EeRSO and 7 % of EKO.

PLA with 3 % of bio-based plasticizer includes EPO and EPSO, while both EKO and EeRSO are at the value of 2.5 % of bio-based plasticizer. In contrast, EPO and EPSO use 7 % bio-based plasticizer and 7.5 % bio-based plasticizer for EeRSO. Based on the graph, the highest tensile strength was observed at Pure PLA. The lowest tensile strength was at PLA was 10 % of bio-based plasticizer, which is applicable for all types of bio-based plasticizer. It can be concluded that as the percentage of bio-based plasticizers increases, the tensile strength decreases.

The reductions of tensile strength occurred as the content of bio-based plasticizer increases is due to the plasticizer-plasticizer interaction in the polymer matrix. The plasticizer-plasticizer interaction, which occurs at a higher percentage of bio-based plasticizers, is the reason for the decrease in tensile strength, resulting in a phase-separated structure (Thuy et al., 2018).

EPO and EPSO show slight increments at 1 %, indicating that the tensile strength improved before decreasing to 10 %. As a result, a minimum of 1 % of EPO and EPSO can improve the tensile strength. Furthermore, a plasticizer is present at the interfacial area at more extensive bio-based plasticizer contents. Simultaneously, the balance is distributed throughout the matrix, affecting homogeneity and resulting in a decrease in the tensile strength of PLA (Chieng et al., 2014).

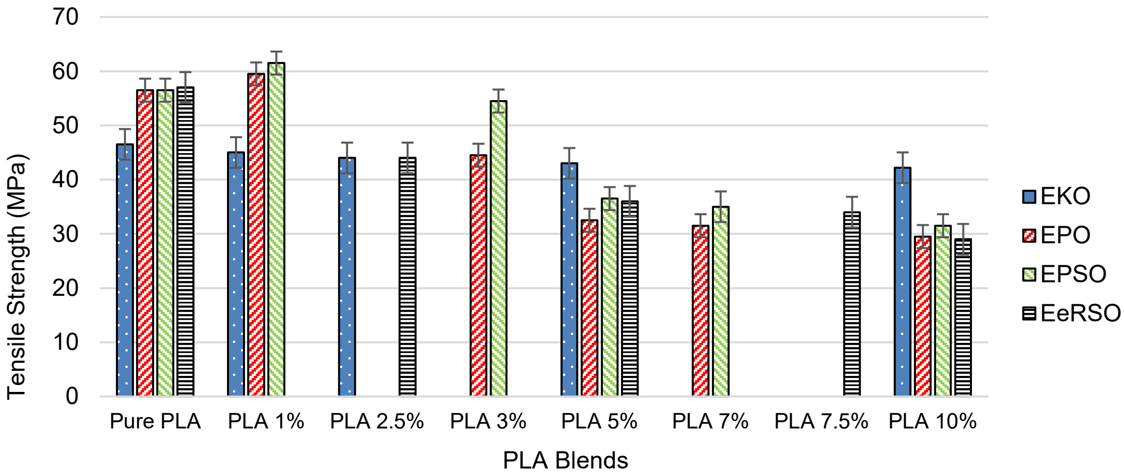


Figure 2: Tensile strength for EKO (Garcia-Garcia et al., 2020), EeRSO (Thuy et al., 2018), EPO, and EPSO (Chieng et al., 2014)

Figure 3 shows the elongation at break for EKO (Garcia-Garcia et al., 2020), EeRSO (Thuy et al., 2018), EPO, and EPSO (Chieng et al., 2014). No data is provided for 1 % of EeRSO and 7 % of EKO like the tensile strength. 3 % of bio-based plasticizer for EPO and EPSO, while for EKO and EeRSO are at the value of 2.5 % of bio-based plasticizer. For 7 % bio-based plasticizer, only EPO and EPSO were demonstrated, and 7.5 % bio-based plasticizer for EeRSO.

The graph indicates pure PLA has the lowest elongation at break, and the highest is at PLA with 5 % of bio-based plasticizer. It shows a significant improvement of 5 % of bio-based plasticizers. Consequently, adding more bio-based plasticizers causes the elongation at break to decrease, making the polymer more brittle (Chieng et al., 2014).

However, for EPSO bio-based plasticizer, it is reported that the highest elongation at break was observed at 7 % of bio-based plasticizer and hence reducing at 10 % of EPSO. This scenario points out that 7 % of EPSO is a sufficient amount of bio-based plasticizer to improve PLA flexibility. As a result, plasticizer reduces intermolecular interactions by stimulating more free volume (Tee et al., 2016). Plasticizers improve PLA polymer chains' mobility, resulting in enhancing the flexibility and extensibility of the PLA blends. In conclusion, PLA with a higher bio-based plasticizer minimizes tensile strength but maximizing elongation. Hence the flexibility nas ductility are enhanced. (Giita Silverajah et al., 2012).

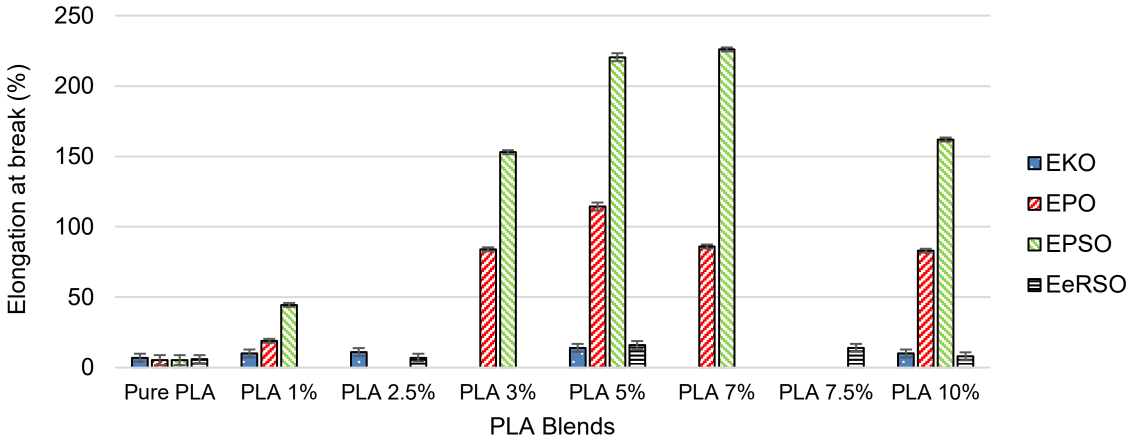


Figure 3: Elongation at the break for EKO (Garcia-Garcia et al., 2020), EeRSO (Thuy et al., 2018), EPO, and EPSO (Chieng et al., 2014)

As shown in Figure 4, two samples were observed on the impact energy; EKO and EeRSO. No data for PLA with 1 % EeRSO and 7 % EKO. Pure PLA has the lowest impact energy. In contrast, 5 % of bio-based plasticizer PLA has the highest impact strength before decreasing 10 %. The impact energy for PLA with EeRSO bio-based plasticizer was approximately zero indicates a huge difference compared to PLA with EKO bio-based plasticizer. The addition of bio-based plasticizers in the PLA matrix significantly increases the ductility and impact strength due to elongation at break (Thuy et al., 2021).

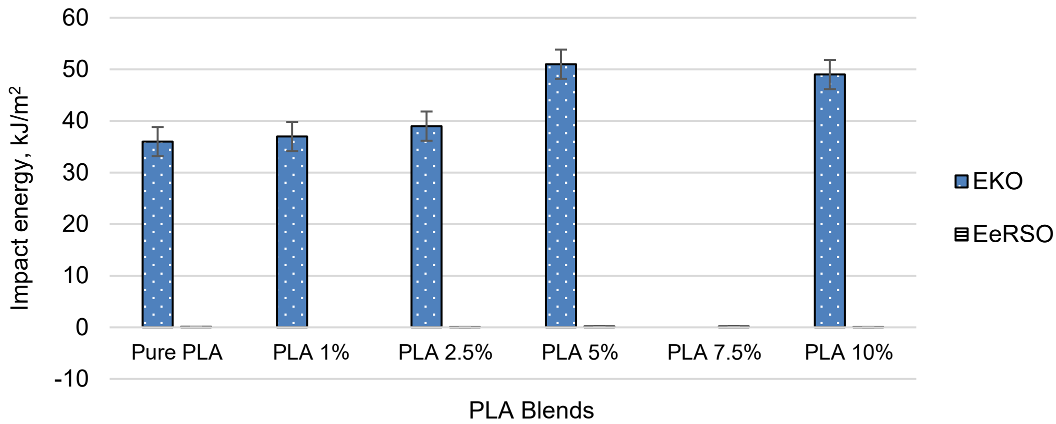


Figure 4: Impact energy for EKO (Garcia-Garcia et al., 2020), EeRSO (Thuy et al., 2018), EPO, and EPSO (Chieng et al., 2014)

3. Conclusions

In this paper, the mechanical properties of PLA and plasticized PLA has been reviewed. Plasticizers improve the mechanical properties of PLA. The elongation at break and impact energy is enhanced to 15 % and 35 %, respectively, which increases flexibility and durability. The optimal blend is 5 % of bio-based plasticizers blended with PLA. This review provides the best evidence for replacing petroleum-based plasticizers with biodegradable and renewable bio-based plasticizers from vegetable oil. Further analysis should focus on Waste Cooking Oil (WCO) or palm oil as the feedstock for bio-based plasticizers. WCO as bio-based plasticizers promotes excellent benefits over conventional plastic, especially towards the environment.

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